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(54) Polyethylene resin composition

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SPECIFICATION

1. Title of the Invention
Polyethylene resin composition

2. Claims

A polyethylene resin composition that is suitable for blow molding and extrusion molding, has excellent environmental stress cracking resistance, with a melt index of 0.05-2.0 g/10 minutes and a density of 0.930-0.960 g/cm³, and consists of a mixture of

(A) 10-65 wt% an ethylene copolymer obtained by polymerizing ethylene and an α -olefin having four or more carbon atoms in the presence of hydrogen and a catalyst system that includes at least one species from among chromium compounds and titanium compounds, substantially without removing the catalysts and low-molecular-weight polymers, that has a density of 0.91-0.95 g/cm³, whose number of branches per 1000

skeletal carbon atoms is 2 or more, that has a degree-of-branching distribution such that the ratio between this and the number of branches per 1000 skeletal carbon atoms of boiling cyclohexane extraction residue is in the range from 1:1 to 1:0.1, and whose limiting viscosity measured in tetralin at 130°C is 2.5-8.2 dl/g, and

(B) 90-35 wt% an ethylene polymer obtained by polymerizing ethylene alone or ethylene and an α -olefin in the presence of hydrogen and a catalyst system that includes at least one species from among chromium compounds and titanium compounds, substantially without removing the catalysts and low-molecular-weight polymers, that has a density greater than 0.955 g/cm³, and whose limiting viscosity measured in tetralin at 130°C is no greater than 1.7 dl/g.

3. Detailed Description of the Invention

This invention concerns a polyethylene resin composition; more specifically, it concerns a polyethylene resin composition that is suitable for blow molding and extrusion molding, has improved environmental stress cracking resistance (hereafter abbreviated as ESCR), and consists of a mixture of a relatively low-molecular-weight ethylene homopolymer or a copolymer of ethylene and an α -olefin that has a high density of 0.955 or more, and a relatively high-molecular-weight low-density copolymer of ethylene of density 0.91-0.95 and an α -olefin that has four or more carbon atoms.

Polyethylene is used in a broad variety of applications, but if used in applications such as pipes or bottles, these molded products tend to break when used over a long period of time, which is a major impediment to its practical use. In this phenomenon, which is known as environmental stress cracking, cracking occurs over a relatively long time period if the molded product is subjected to external stress or if strain remains from when it was molded. And depending on the environmental conditions under which the molded products are used, this phenomenon sometimes becomes more pronounced.

Among the methods that have been proposed for improving the ESCR of polyethylene are the method of blending into the polyethylene a rubber, such as natural rubber, SBR [styrene-butadiene rubber], butyl rubber, or EPR, and the method of blending in polybutene-1, polycarbonate, ethylene-vinyl acetate copolymer, and low-molecular-weight, low-melting-point paraffin wax. But these methods are unsatisfactory for practical use as resin compositions for blow molding and extrusion molding in some or all of the following points.

- (1) Their ESCR is still not satisfactory for practical use.
- (2) The mechanical properties of the molded products, in particular their rigidity, decline.
- (3) The mixtures dissolve out at low temperature in certain solvents.
- (4) The blended materials are expensive and uneconomical.

Also known as methods for improving the ESCR of polyethylene without mixing in other polymers as above are the method of lowering the density by copolymerizing ethylene and an α -olefin such as propylene or butene-1, the method of increasing the molecular weight (which in general makes the melt index smaller), and improvement methods by grafting, crosslinking, etc. But these methods still yield an inadequate ESCR, lower the mechanical properties, or have low fluidity during molding, which is an impediment for some applications, and these methods are often not of practical utility.

With the increasing uses and demand for polyethylene in recent years, even greater performance has come to be wanted, and the demanded performance differs from one application to another. Among the physical properties demanded of polyethylene for use in blow molding and extrusion molding are (1) good ESCR, (2) high density and excellent mechanical properties, in particular, high rigidity, (3) good processing characteristics, and (4) fixed quality.

In general, the ESCR of polyethylene improves with lower density or with a lower melt index and higher molecular weight. But rigidity and other mechanical strength characteristics decline if the density is reduced. On the other hand, reducing the melt index (increasing the molecular weight) worsens the fluidity during processing and makes processing considerably more difficult. Thus there is a tradeoff between (1) improving the ESCR and (2) having a high density and (3) having good processing characteristics, especially fluidity during processing.

As a result of various study to solve these difficult problems and come up with a polyethylene resin composition that is suitable for blow molding and extrusion molding, the inventors arrived at this invention having learned that a polyethylene resin composition that is very suitable for blow molding and extrusion molding, with a good balance of ESCR, density, and workability, having a melt index of 0.05-2.0 and a density of 0.930-0.960, results from a mixture consisting of

(A) 10-65 wt% an ethylene copolymer obtained by polymerizing ethylene and an α -olefin having four or more carbon atoms in the presence of hydrogen and a catalyst system that includes at least one species from among chromium compounds and titanium compounds, substantially without removing the catalysts and low-molecular-weight polymers, that has a density of 0.91-0.95, whose number of branches per 1000 skeletal carbon atoms is 2 or more, that has a degree-of-branching distribution such that the ratio between this and the number of branches per 1000 skeletal carbon atoms of boiling cyclohexane extraction residue is in the range from 1:1 to 1:0.1, and whose limiting viscosity measured in tetralin at 130°C is 2.5-8.2, and

(B) 90-35 wt% an ethylene polymer obtained by polymerizing ethylene alone or ethylene and an α -olefin in the presence of hydrogen and a catalyst system that includes at least one species from among chromium compounds and titanium compounds, substantially without removing the catalysts and low-molecular-weight polymers, that has a density greater than 0.955, and whose limiting viscosity measured in tetralin at 130°C is no greater than 1.7 dl/g.

In the following we describe the content of this invention in greater detail. The inventors have previously proposed an accurate, reproducible ESCR evaluation method and device (unexamined patent S52-109988 [1977]). The inventors learned the following facts as a result of various examinations of the ESCR of olefin polymers and olefin polymer compositions conducted according to working example 1 of this unexamined patent S52-109988 [1977].

1. ESCR is additive if two olefin polymers that have a different ESCR are mixed together. For example, as shown in Figure 1, if polyethylene A (melt index 0.53, density 0.944, ESCR F_{50} 202) and polyethylene B (melt index 8.1, density 0.962, ESCR F_{50} 8.4) are mixed together, then the logarithm of the F_{50} value of the mixture (the time until 50%

of the 10 test samples break, an index of how good the ESCR is) will agree with the sum of the products of the logarithms of the F_{50} values of the components with their weight proportions.

2. In the case of a single olefin polymer, the ESCR of a copolymer of ethylene and an α -olefin is better than the ESCR of an ethylene polymer that has the same molecular weight. Also, the ESCR of a copolymer of ethylene and an α -olefin differs with the types of comonomers used, even if their molecular weights and densities are the same, and the larger the carbon number of the monomers, the better the ESCR of the copolymer. For example, as shown in Table 1, if we compare ethylene/propylene copolymer, ethylene/butene-1 copolymer, and ethylene/hexene-1 copolymer, which have roughly the same limiting viscosity and density, the ESCR of the copolymers is better in sequence ethylene/propylene copolymer, ethylene/butene-1 copolymer, and ethylene/hexene-1 copolymer. That is, if an α -olefin whose carbon number is 4 or more, such as butene-1 or hexene-1, is used as the comonomer, the ESCR of the polyethylene copolymer will be dramatically improved. But if the comonomer is propylene, its proportional improvement will be small.

Table 1

	Limiting viscosity	Density	ESCR F_{50} (hours)
Ethylene/propylene copolymer	2.40	0.940	105
Ethylene/butene-1 copolymer	2.12	0.944	202
Ethylene/hexene-1 copolymer	2.42	0.940	435
Ethylene-only polymer	2.51	0.958	21

*Density: measured by JIS K-6760.

3. A copolymer of ethylene and an α -olefin has a better ESCR the higher its molecular weight is. For example, as shown in Figure 2, a low-molecular-weight copolymer, even if its degree of branching (the number of branches per 1000 carbon atoms, which normally corresponds to the copolymer's proportion of comonomers) is increased, does not show much improvement in ESCR over a homopolymer denoted by a degree of branching 0, and conversely, a high-molecular-weight copolymer shows a dramatic improvement in ESCR even if its degree of branching is small. Moreover, measurement of short-chain branches was done by the infrared absorption spectrum method, and by the Willbourn method by the absorption of the methyl group at 1378 cm^{-1} , taking the absorption at 4255 cm^{-1} as an internal standard (see A. H. Willbourn, *Journal of Polymer Science*, volume 34, page 569 (1959)).

Also, those for which F_{50} , which is an index of how good the ESCR is, is 1000 hours or more are mixed with polyethylene, whose F_{50} is 8.4 hours, and the determination is made by calculation from the F_{50} of the mixture according to the above-described additivity.

4. Although closely related with the facts described in 3, the distribution of short-chain branches with respect to molecular weight (the degree-of-branching distribution) is closely related to the ESCR, and the more branches there are in the high-molecular-weight part of the olefin copolymer, the better the ESCR is.

Table 2

	Limiting viscosity	Density	Degree of branching	Degree of branching of boiling cyclo- hexane extrac- tion residue	Ratio	ESCR F_{50} (hours)
Ethylene/ butene-1 copolymer A	2.10	0.938	4.6	4.2	0.91	365
Ethylene/ butene-1 copolymer B	2.15	0.943	10.5	0.8	0.08	52

* Boiling cyclohexane extraction residue means what results when polymer powder is extracted for 6 hours with boiling cyclohexane, then what remains unextracted is dried under reduced pressure for 20 hours at 80°C.

For example, as shown in Table 2, ethylene/butene-1 copolymer B, whose low-molecular-weight part extracted in boiling cyclohexane has many branches and whose extraction residue has few branches, has a worse ESCR than ethylene/butene-1 copolymer A, whose extraction residue has many branches. Also, copolymers A and B listed in Table 2 were fractionated by molecular weight by column fractionation, and their distribution of degree of branching with respect to molecular weight (degree-of-branching distribution) was determined. The details of the column fractionation technique are given by J. H. Elliot in "Polymer Fractionation," edited by M. J. R. Cantow, pages 67-93 (published 1967 by Academic Press); to briefly describe the technique below, an approximately 5-g sample is deposited as a carrier on Cellite 545 in xylene, then the column is filled with it. Next, the column is heated to 126°C, and it is allowed to flow down the column while varying the butyl cellosolve-xylene mixing ratio, and the high-molecular-weight portion is successively separated from the low-molecular-weight portion. Methanol is added to the effluent, the polymer that precipitates is

recovered, then the fraction is separated by reduced-pressure drying. The molecular weight (M) of the resulting fractioned portion is measured by the following formula according to the limiting viscosity ($[\eta]$) measured in tetralin at 130°C.

$$[\eta] = 4.71 \times 10^{-4} M^{0.71}$$

Also, the degree of branching of the fractioned portion was determined by the infrared absorption spectrum method referred to above. Figure 3 shows the degree-of-branching distribution of copolymers A and B of ethylene and butene-1 determined in this way. As shown in Figure 3, while the degree-of-branching distribution of copolymer A, which has good ESCR, is uniform and there are many branches even in the portion having a molecular weight of 100,000 or more, in copolymer B, which has bad ESCR, the degree-of-branching distribution is non-uniform, there are almost no branches in the portion having a molecular weight of 100,000 or more, showing that the branches in the high-molecular-weight portion dramatically improve the ESCR.

The above knowledge is what led to this invention, but the high-molecular-weight, low-density ethylene copolymer used in this invention (hereafter abbreviated as component A) is a copolymer of ethylene and an α -olefin that has four or more carbon atoms, and its density should be 0.91-0.95. And because manufacturing an ethylene copolymer whose molecular weight is too high makes it prone to gelling and makes it difficult to mix with other polyolefins, its limiting viscosity should be 2.5-8.2, and preferably 3.0-6.5. And if an ethylene copolymer made without hydrogen in the presence of a catalyst system that includes at least one species from among chromium compounds and titanium compounds is mixed with another polyolefin, the composition will show too great a ballast effect, and if used for blow molding and extrusion molding, it will have poor workability, including poor high-speed workability, difficulty in parison control, and difficulty in producing complicated shapes, so it is desirable that the copolymer be manufactured in the presence of hydrogen.

Also, a copolymer with an uneven degree-of-branching distribution is undesirable, because it includes many branches in its low-molecular-weight portion, which has little effect on improving the ESCR, and because this lowers the density to no good purpose. Therefore what is used is one that has two or more branches per 1000 skeletal carbon atoms and has a degree-of-branching distribution in which the ratio between this and the number of branches per 100 skeletal carbon atoms of boiling cyclohexane extraction residue is in the range of preferably 1:1 to 1:0.1, and more preferably 1:1 to 1:0.5.

Such copolymers are obtained by copolymerizing ethane with an α -olefin such as butene-1, pentene-1, 4-methyl pentene-1, hexene-1, or octene-1 in the presence of hydrogen and a catalyst of the medium-pressure or low-pressure method, especially a carrier-bearing catalyst that copolymerizes uniformly up to the high-molecular-weight components.

As such catalyst systems we can cite the so-called Phillips type catalysts or Ziegler type catalysts. Specific examples that can be cited include catalysts that have silica or silica alumina as their carrier and that carry 0.5-6 wt% chromium oxide; those that carry a titanium halide, such as titanium tetrachloride or titanium trichloride, on a magnesium compound such as magnesium chloride, magnesium alkoxide, or magnesium hydroxide, or reaction products of these; catalysts whose main component is an organic aluminum compound such as triethyl aluminum or triisobutyl aluminum; and catalysts whose main

components are reaction products of titanium tetrachloride and metal aluminum, and organic aluminum compounds, etc.

On the other hand, the low-molecular-weight, high-density ethylene copolymer used as the other component in this invention (hereafter abbreviated as component B) can be manufactured by polymerizing ethylene alone or ethylene and an α -olefin by a well known medium-pressure or low-pressure method in the presence of hydrogen and a catalyst system that includes at least one species from among chromium compounds and titanium compounds. This component B should have a density of 0.955 or more and a limiting viscosity of no more than 1.7. More preferably, it should have a density of 0.960 or more and a limiting viscosity of no more than 1.5. If its density is less than 0.955, the density of the composition will be low, and it will be impossible to obtain a good composition with high rigidity and other mechanical strength.

And if the limiting viscosity is 1.7 or more, it will be impossible to obtain a composition that has good fluidity during processing.

The polyethylene resin composition of this invention formed by mixing such components A and B should, in order to be used for blow molding and extrusion molding, have a melt index, as measured according to JIS K-6760, in the range from 0.05 to 2.0, and should have a density of 0.930-0.960, and preferably 0.940-0.960.

This invention imposes no particular limitation on the mixing method when manufacturing the polyethylene resin composition; any of various mixing methods that provide a uniform composition can be used, such as the method of manufacturing components A and B individually and then mixing them with a mixing machine, or the method of mixing them inside the reaction vessel by polymerizing one component, then polymerizing the other component with the same catalysts (the two-stage polymerization method). The mixing ratio and combination of components A and B are closely related with the ESCR, density, and workability of the composition; in particular, the density is expressed roughly by the following formula, and is proportional to the mixing ratio.

$$\frac{1}{d} = \frac{1}{d_A} W_A + \frac{1}{d_B} W_B$$

(where d , d_A , d_B are the density of the composition, of component A, and of component B, respectively, and W_A and W_B are the proportions by weight of components A and B, respectively; $1 = W_A + W_B$).

Therefore in the mixing ratio of components A and B, a desirable combination is one in which high-limiting-viscosity component A makes up 10-65 wt% of the composition as a whole, the difference in density between components A and B is at least 0.01, and preferably at least 0.02, and the limiting viscosity of component A is at least 1.5 times, and preferably at least 2 times, the limiting viscosity of component B.

If the thus obtained polyethylene resin composition of this invention is used in blow molding and extrusion molding, because of its superior ESCR, there is no danger of environmental stress failure, and because of its high density, its mechanical strength is high, with especially good rigidity, allowing the molded products to be made thin. In addition, the wide distribution of molecular weight in the resin composition gives it good fluidity during processing. That is, a large extrusion quantity can be obtained at low

pressure, and even when processing is done at a high extrusion speed, there is no danger of roughness occurring on the surface of the molded products.

Ordinary additives can be added to the composition of this invention, including antioxidants, antistatic agents, ultraviolet absorption agents, color pigments, and lubricants.

In the following, we describe this invention in greater detail through working examples, but this invention is not limited to the following working examples, provided that its gist is not exceeded.

Also, the effluent ratio in the working examples and comparison examples is defined as the ratio of the quantity of effluent when a 21.60-kg load is applied, to the quantity of effluent when a 2.16-kg load is applied, in the melt index measurement method prescribed in JIS K-6760. This effluent ratio is an index expressing the degree to which the flow is dependent on the pressure: when this value is high, the fluidity at high pressure is superior, and melt fracture will not occur up to a high rate of shear. Also, the swelling ratio is an index for the ballast effect; it is expressed by the ratio of the diameter of the extruded strand to the diameter of the orifice when the melt index is measured. The F_{50} of ESCR is measured by the method and device described in working example 1 of unexamined patent S52-109988 [1977]; it is approximately 2.8 times the value obtained by the Pentstop[?] method prescribed in ASTM D-1693-70.

Working example 1

Crushed together in a vibrating ball mill were 20 g of anhydrous magnesium chloride and 6 g of benzoyl chloride. Then 15 g of the resulting crushed-together material was put into a 500-ml flask, and a solvent was added that was obtained by previously mixing and reacting at room temperature 125 ml of toluene, 86.3 g of titanium tetrachloride, and 12.4 g of dimethyl dimethoxy silane. The crushed-together material and the mixed reaction solution were stirred and mixed for 2 hours at a temperature of 65°C. The resulting solid component was filtered out and washed with toluene, then a powdery catalyst component was obtained by drying at 40°C under reduced pressure. Then 20.1 mg of this catalyst component, 0.54 g of triethyl aluminum, 1 kg of isobutene, 0.09 g of hydrogen, and 18.2 g of butene-1 were put into a 3-liter autoclave. The autoclave was heated to 85°C, and the ethylene was polymerized for 80 minutes while maintaining its partial pressure at 10 kg/cm². Following completion of the polymerization, the monomers and solvent were distilled off under heating, and the sample was used as is, without particularly removing the catalysts and low-molecular-weight components. The same treatment was also carried out in the following working examples and comparison examples. The thus obtained copolymer of ethylene and butene-1 had a limiting viscosity of 6.2, a density of 0.915, a degree of branching of 14.8 per 1000 C, and a degree of branching of boiling cyclohexane extrusion residue of 13.5 per 1000 C, for a ratio of 1:0.91.

On the other hand, ethylene was homopolymerized by the same method as above, except that butene-1 was not used, and the hydrogen was increased to 0.31 g. The resulting polyethylene had a limiting viscosity of 1.2 and a density of 0.962.

The resulting 25 wt% copolymer of ethylene and butene-1 and 75 wt% polyethylene was roll-kneaded and mixed for 10 minutes at 145°C. When the physical properties of

the resulting polyethylene resin composition were measured, the results listed in Table 3 were obtained.

Table 3

Melt index	0.22
Flow ratio	103
Swelling ratio	1.31
Density	0.950
ESCR (F ₅₀)	no breakage at 2000 hours

Working example 2

Silica alumina carrier was made to carry 1 wt% chromium oxide, 105 mg of chromium oxide-silica alumina catalyst activated in the atmosphere for 10 hours at 700°C, 500 g of isobutane, 28.8 g of hexene-1, and 0.15 g of hydrogen were put into a 1.5-liter autoclave and heated to 90°C. Then ethylene was polymerized for 1 hour while maintaining its partial pressure at 23 kg/cm². The resulting copolymer of ethylene and hexene-1 had a limiting viscosity of 3.9, a density of 0.928 g/cm³, and a degree of branching of 8.1 per 1000 C, with the degree of branching of the boiling cyclohexane extraction residue being 7.5 per 1000 C, for a ratio of 1:0.92. On the other hand, silica alumina carrier was made to carry 2 wt% chromium oxide, 232 mg of chromium oxide-silica alumina catalyst activated in the atmosphere for 10 hours at 850°C, 1 kg of cyclohexane, and 0.35 g of hydrogen were put into a 3-liter autoclave. Next, it was heated to 160°C, and 350 g of ethylene was pressed in and polymerized while maintaining its partial pressure at 10 kg/cm². The resulting polyethylene had a limiting viscosity of 0.78 and a density of 0.970.

The resulting 36 wt% copolymer of ethylene and butene-1 and 64 wt% ethylene homopolymer was roll-kneaded and mixed for 10 minutes at 145°C. When the physical properties of this polyethylene resin composition were measured, the results listed in Table 4 were obtained.

Table 4

Melt index	0.11
Flow ratio	179
Swelling ratio	1.62
Density	0.954
ESCR F ₅₀	285

Comparison example 1

Homopolymerization of ethylene and copolymerization of ethylene and propylene were carried out in the presence of hydrogen with the same catalysts and equipment as used in working example 1. The limiting viscosity of the resulting polyethylene was 6.3. The limiting viscosity of the ethylene/propylene copolymer was 7.6, and its density was 0.917. Composition A was obtained by roll-kneading and mixing at 145°C 25 wt% of this polyethylene and 75 wt% of the polyethylene used in working example 1, which had a limiting viscosity of 1.2 and a density of 0.962. In the same way, composition B was obtained by mixing 25 wt% of said ethylene/propylene copolymer and 75 wt% of the polyethylene used in working example 1, which had a limiting viscosity of 1.2 and a density of 0.962. Their physical properties were measured, yielding the results listed in Table 5.

	Table 5	
	Composition A	Composition B
Melt index	0.23	0.10
Flow ratio	98	115
Swelling ratio	1.33	1.21
Density	0.961	0.950
ESCR F ₅₀	31	178

Comparison example 2

Copolymerization of ethylene and butene-1 was carried out, without the presence of hydrogen, with the same catalysts and equipment as was used in working example 1. The resulting copolymer had a limiting viscosity of 11.5 and a density of 0.911. Then 15 wt% of this copolymer and 85 wt% of the polyethylene used in working example 1, which had a limiting viscosity of 1.2 and a density of 0.962, was roll-kneaded for 10 minutes at 145°C. It was found that the resulting composition had a melt index of 3.3 and an ESCR (F₅₀) of 3 hours, with no mixing at all.

Comparison example 3

Titanium tetrachloride, triethyl aluminum, and isobutane were put into a 3-liter autoclave, it was heated to 85°C, and polymerization was carried out, pressing in ethylene, butene-1, and hydrogen up to a total pressure of 26 kg/cm². The resulting ethylene/butene-1 copolymer had a limiting viscosity of 6.5, a density of 0.921, and a degree of branching of 19.8 per 1000 C, with the degree of branching of the boiling cyclohexane extraction residue being 1.6, for a ratio of 1:0.08. Then 25 wt% of this copolymer and 75 wt% of the polyethylene used in working example 1, which had a limiting viscosity of 1.2 and a density of 0.962, were mixed by the same method as in working example 1. This composition was measured, yielding the results of Table 6.

Table 6

Melt index	0.19
Flow ratio	110
Swelling ratio	1.30
Density	0.951
ESCR F ₅₀	41

It is clear that a large difference in ESCR arises if the distribution of degree of branching is different, even if it is a composition in which the conditions are the same as in working example 1.

Working examples 3-9

A catalyst component was obtained by reacting in toluene the reaction products of titanium tetrachloride and tetraethoxy silane in the crushed-together material made by crushing together and treating anhydrous magnesium chloride and trichloroacetyl chloride. This catalyst and triethyl aluminum were taken as cocatalysts, and copolymerization of ethylene was carried out by the same method as in working example 1. However, the comonomers used were varied as shown in Table 7.

Table 7

	Comonomer	Limiting viscosity	Density	Degree of branching	Degree of branching of cyclohexane extraction residue	Ratio of degree of branching
Copolymer 1	Butene 1	2.75	0.932	6.3	5.9	0.94
Copolymer 2	Butene 1	3.45	0.929	7.1	6.5	0.92
Copolymer 3	Hexene 1	6.21	0.916	8.7	7.2	0.83
Copolymer 4	Hexene 1	3.24	0.932	4.6	4.2	0.91

The copolymers in Table 7 and the polyethylene of limiting viscosity 0.78 and density 0.970 used in working example 2 were mixed by rolls in the proportions listed in Table 8. When the physical properties of the resulting compositions were measured, the results listed in Table 8 were obtained.

Table 8

Working example	Co-poly-mer	Proportion of copoly- in compo- sition (wt%)	Melt index	Flow ratio	Swelling ratio	Density	ESCR F ₅₀
3	1	40	1.5	47	1.58	0.954	98
4	2	30	0.91	89	1.68	0.957	125
5	"	40	0.38	118	1.75	0.953	440
6	3	27	0.22	419	1.82	0.954	2000 hr no break
7	"	15	1.8	72	1.89	0.960	269
8	4	50	0.51	59	1.46	0.950	225
9	"	60	0.30	60	1.44	0.947	480

4. Brief Explanation of the Drawings

Figure 1 shows examples in which ESCR is additive if polyethylene A and polyethylene B, which each have a different ESCR, are mixed together; Figure 2 shows the relationship between the ESCR and the degree of branching, which depends on the difference in molecular weight of the ethylene copolymers; and Figure 3 shows the relationship between the ESCR and the molecular weight of ethylene and butene-1 copolymers of different ESCR.

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Figure 1

[horizontal axis:] Polyethylene A Mixing ratio Polyethylene B

Figure 2

[horizontal axis:] Degree of branching ($-C_2H_5$ groups/1000 C)

Figure 3

[vertical axis:] Degree of branching ($-C_2H_5$ groups/1000 C)

[horizontal axis:] Molecular weight (M)

[upper curve:] Copolymer A

[lower curve:] Copolymer B